



Review

Recent advances in lithium–sulfur batteries

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HIGHLIGHTS

- Li–S batteries have great potential as the next generation high capacity batteries.
- Nanostructured sulfur electrodes are essential to realize this potential.
- Anodes, electrolytes, additives, binders and separators also play critical roles.
- Cell configuration with novel components can result in breakthroughs.

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ABSTRACT

Lithium–sulfur (Li–S) batteries have attracted much attention lately because they have very high theoretical specific energy (2500 Wh kg^{−1}), five times higher than that of the commercial LiCoO₂/graphite batteries. As a result, they are strong contenders for next-generation energy storage in the areas of portable electronics, electric vehicles, and storage systems for renewable energy such as wind power and solar energy. However, poor cycling life and low capacity retention are main factors limiting their commercialization. To date, a large number of electrode and electrolyte materials to address these challenges have been investigated. In this review, we present the latest fundamental studies and technological development of various nanostructured cathode materials for Li–S batteries, including their preparation approaches, structure, morphology and battery performance. Furthermore, the development of other significant components of Li–S batteries including anodes, electrolytes, additives, binders and separators are also highlighted. Not only does the intention of our review article comprise the summary of recent advances in Li–S cells, but also we cover some of our proposals for engineering of Li–S cell configurations. These systematic discussion and proposed directions can enlighten ideas and offer avenues in the rational design of durable and high performance Li–S batteries in the near future.

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1. Introduction

Lithium-ion batteries (LIBs), one of common rechargeable power sources, have dominated in portable device markets for more than 20 years since their initial launch in 1990s. However, LIBs which nearly reach their theoretical capacity [1,2] and leave little room for further exploration cannot meet the current need for applications in systems such as electric vehicles that require large capacity and long battery cycle life [3]. With increasing demand and immense market potential [4], rechargeable batteries with superior

energy density and low cost are thus always urgently searched in academia and industrial world [5–10].

Metallic lithium has a very high electronegativity while possessing the lowest density among all metals, leading to its highest specific capacity (3861 mAh g^{−1}) and thus has been considered to be the best candidate for rechargeable battery anodes [11]. Element sulfur has a theoretical capacity of 1673 mAh g^{−1} [12]. Thus, Li–S batteries can reach unparalleled gravimetric and volumetric energy densities of 2500 Wh kg^{−1} and 2800 Wh L^{−1}, respectively, assuming a complete reaction to Li₂S [13]. Also, they are cheaper compared to conventional LIBs owing to highly abundant sulfur storage in the earth. Further, the sulfur cathode can operate at a safer voltage range (1.5–2.5 V vs. Li/Li⁺). Another advantage of sulfur is its non-toxicity. Undoubtedly, all of these advantages make Li–S cells an excellent alternative for energy storage and could play an important role in diversifying energy sources as well as utilizing

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renewable energy, thereby alleviating global warming and reducing the use of fossil fuels.

However, commercialization of Li–S batteries has been gravely hindered by several issues, such as the insulating nature of sulfur element ($\sim 5 \times 10^{-30} \text{ S cm}^{-1}$ at 25°C) [14] and polysulfide dissolution causing active sulfur loss and rapid capacity fading. In order to address these challenges, many endeavors have been made to fabricate materials into nano-dimensions and nanostructures, which are considered as effective solutions to solve the problems owing to their more resistance to structural degradation by virtue of materials' nanoscale sizes [15]. Also, nanostructured materials with incorporation of carbon nanotubes and nanofibers can enhance the rate capability because the path for ionic and electronic conductivity is shortened. On basis of these thoughts, nanostructures can be very significant in circumventing some challenges of the Li–S system. Although nanostructured materials are not easy to prepare and many challenges still need to be overcome, researchers who are interested in Li–S systems have already made significant advancements. In spite of the tremendous progress, however, there are only several reports on lithium sulfur batteries with good capacity performance up to 1000 cycles [12,16], which is required by the US Department of Energy for electric vehicle grade battery systems [17]. Given the great potential of the Li–S system, a comprehensive review of the recent advances in the Li–S system is warranted.

Several reviews of Li–S batteries have been published recently [13,18–24]. However, most of these reviews emphasize the recent progress in cathode research, whereas the advancements and challenges associated with anodes, electrolytes, additives, binders, and separators are little mentioned [13,18–23] or partially discussed [24]. In this review, we will cover all of these topics to provide a comprehensive overview of the challenges and advancements in various components of Li–S batteries. We will first discuss the working process of Li–S rechargeable batteries. We will then present the latest fundamental studies and technological development of various nanostructured cathode materials for Li–S batteries, including their preparation approaches, structure, morphology and battery performance. The development of other significant components of Li–S batteries such as anodes, electrolytes, additives, binders and separators will be subsequently summarized. Finally, based on the experiment exploration conducted to date, we will discuss the significant lessons and propose future directions that can be focused on. Not only does the intention of our review article include the comprehensive summary of recent advances in Li–S cells, but also we cover our ideas for some designs of Li–S cell configurations. We hope that the systematic review and proposed avenues can enlighten discussion and provide directions for developing durable and high performance Li–S batteries in the near future.

2. Lithium–sulfur battery operation and challenges

2.1. Operation and SEI formation

A lithium–sulfur battery encompasses three major components: a cathode, an anode and a non-aqueous electrolyte. The anode and cathode are typically separated by a porous separator soaked with the non-aqueous electrolyte, allowing ions but preventing electrons to pass through to avoid short circuit. Fig. 1 shows a schematic representation of the working process of a Li–S battery. The anode (negative electrode) and cathode (positive electrode) are connected to an external circuit. Upon discharging, Li ions from the anode diffuse to the cathode, while the electrons move from the anode through the external circuit to the cathode. It is known that sulfur in the cathode exists in the form of a large molecule, i.e., a

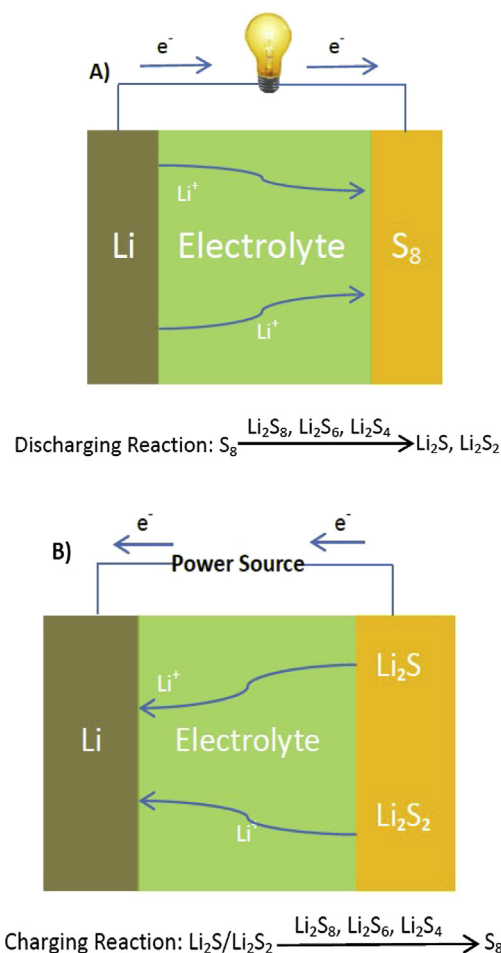


Fig. 1. Schematic presentation of a lithium–sulfur battery with the anode (metallic lithium) and cathode (sulfur-containing material), separated by a non-aqueous liquid electrolyte. A) Discharging process and B) charging process.

cyclooctasulfur S₈; thus, sulfur cannot turn into Li₂S in one-step reaction. Instead, when lithium ions from the anode react with the sulfur cathode, long-chain lithium polysulfides (Li₂S_x, $4 \leq x \leq 8$) [25,26], which are soluble intermediate products, are generated at the initial stage. These long-chain polysulfides will turn into insoluble Li₂S₂ and finally Li₂S with further discharging [27]. During this discharge process, negatively charged polysulfides dissolving in the liquid organic electrolyte also undergo shuttle moving driven by chemical potential and concentration difference between the cathode and the anode. Mikhaylik et al. [28] have reported a quantitative study of this shuttle phenomenon in the Li–S system. Their work shows that discharge curves of the Li–S cell at room temperature constitute two voltage plateaus, which are 2.3–2.4 V and ~2.1 V, corresponding to accepting 0.5 electron per sulfur atom with lithium tetrasulfide (Li₂S₄) as the product and accepting an additional electron per sulfur atom with lithium sulfide (Li₂S) and disulfide (Li₂S₂) mixture as the products, respectively, consistent with other reports [29,30].

Charging is a reverse process of discharging. In this process, external power source forces electrons to move from the cathode to the anode through an external circuit, while lithium ions diffuse through the separator back to the anode as shown in the schematic of Fig. 1b.

In addition to the key electrochemical reactions during charging and discharging described above, other processes could take place at the same time to impact the Li–S battery performance. These

side reactions will be discussed in Section 2.2. Furthermore, it is important to emphasize that the solid electrolyte interphase (SEI) layer can also be formed on the lithium anode surface of the Li–S batteries, although this topic is often overlooked by many reports. Lithium ions can pass through the SEI layer to reach the anode, while the stable SEI layer prevents the anode from reaction with polysulfides in the electrolyte [31]. The SEI layer is therefore very beneficial to the overall capacity and coulombic efficiency of the Li–S battery.

2.2. Challenges for Li–S cells

Lithium–sulfur batteries have been studied for more than four decades since late 1960s [32]. Despite significant advancement in this area, there are still challenges remaining thorny and unsolved. The first is associated to the insulating nature of sulfur and its electrochemical products that only allow ions and electrons to diffuse on their surfaces. Thus, some conductive materials have to be mixed with sulfur in the cathode to impart conductivities. Second, polysulfides as discharge intermediate products can dissolve into the organic electrolyte, which reduces sulfur active materials in the cathode [27,32]. The dissolved polysulfides can also diffuse to the lithium anode driven by chemical potential and concentration difference between the cathode and the anode, be reduced to Li_2S and Li_2S_2 , and deposit on the lithium anode [33], leading to undesired parasitic reactions. This deposit increases the resistance of ion conductivity in the anode, and could result in penetration of the cell membrane if the insoluble compound continues to grow, leading to safe issues of the battery. The last major problem for Li–S batteries is the large volume expansion of sulfur as high as ~80% during cycling. Sulfur cathodes experience large volume expansion during discharging and go through volume contraction upon charging. The cathode will be pulverized caused by the internal strain resulting from the volume changes, leading to loss contact between the electrode and current collector and ultimate pulverization with severe capacity fading. Thus, to ensure consistent cycling performance of Li–S systems over several hundreds and thousands of charge/discharge cycles required in practical applications, the three major problems summarized above need to be solved.

Tremendous efforts to address the three main problems described above have been made. Although most of these efforts are focusing on development of novel cathodes via various synthesis methods in making nanostructured cathodes, sulfur allotropes, core–shell structures, and bonding elemental sulfur with conductive substrates, research on other components (such as anodes and electrolytes) has also been conducted. Herein, we intend to highlight that every component, including cathodes, anodes, electrolytes, additives, binders and separators, can be effective in solving the problems. In the following sections, we review various approaches employed by researchers in addressing the three key problems associated with the Li–S system, evaluate their effectiveness, and discuss their advantages for better understanding and rational design of Li–S batteries.

3. Nanostructured sulfur cathodes

Nanoscale and nanostructured sulfur electrodes can be engineered with different morphologies, such as porous carbon–sulfur composites and sulfur-containing nanotubes, to offer more free space to accommodate volume variations during cycling, thereby mitigating internal strain and pulverization to achieve greater cycling stability. The utilization of nanoscale dimensions and nanostructures can also improve rate capability. It is known that the capacity of a cell would decrease at high charge/discharge rates.

Reducing the electrode dimensionality to increase the surface-to-volume ratio can provide shorter pathways for ions and electrons to migrate, beneficial for reduced electrode polarization and high capacity. In addition, the free space within the cathode can host more sulfur, making direct contribution to a higher capacity of the cell.

Excellent sulfur cathodes for high capacity and great cycling stability should contain several desired features, namely: (1) sufficient content of sulfur, (2) good conductivities achieved, for example, by mixing conductive materials in the cathode, (3) flexible structure to buffer the volume change, and (4) methods to trap polysulfides at the cathode. In other words, the desirable cathode should have high content of sulfur with no compromise in superior ionic and electronic conductivities and with resistance to pulverization while retaining the polysulfide intermediates within the electrode.

We will present different nanosized and nanostructured sulfur-based cathodes in this section based on morphologies and compositions of the electrode, including: (1) zero dimension porous carbon–sulfur composites; (2) one dimension sulfur containing nanotubes/nanofibers; (3) graphene–sulfur electrodes; (4) three dimensional (3D) nanostructured sulfur composites; (5) core/yolk–shell structure for sulfur cathodes; (6) polymer–sulfur nanocomposites; and (7) Li_2S cathodes. With such systematic discussion covering almost all of the previous works related to sulfur cathodes, we aim to provide a better and comprehensive understanding in this area.

3.1. Zero dimension porous carbon–sulfur composites

In real world, many plant stems and organisms have porous structures that function as protective cell walls and channels for water uptake [34]. Some of them which are rigid or semi-rigid can be as hard templates for the synthesis of porous materials. Despite prevalent existence of porous structures in nature, it is expensive or difficult to prepare materials with pores, especially with hierarchical or ordered pores. Lately, Stein et al. [34,35] have published reviews emphasizing on how porous materials are designed for applications in batteries through both hard-templating and soft-templating, which are effective routes for the fabrication of ordered porous materials.

Porous materials are classified as micro- (<2 nm), meso- (2–50 nm) and macro- (>50 nm) porous materials. In order to improve the electrical conductivity of the sulfur cathode, housing sulfur within porous carbon materials is a superior option although some other conductive matrixes have also been investigated [36,37]. As a conductive matrix, porous carbon not only hosts sulfur in the pores with high content, but also traps the cycling intermediate polysulfides within pore structures, facilitating the redox reaction while enhancing the capacity retention.

Microporous carbon proves to be an effective sulfur immobilizer because it has very small pores to confine sulfur and prevent intermediate product polysulfides from outflowing into the electrolyte [38]. Zhang et al. [39] have obtained microporous carbon–sulfur composites with an extremely narrow pore size distribution of about 0.7 nm after thermal treatment of sublimed sulfur and carbon spheres, which is formed with sucrose as the source. This material delivers a large reversible capacity of approximately 650 mAh g^{-1} even after 500 cycles at a current density of 400 mA g^{-1} , and displays a coulombic efficiency as high as 100% except for the initial cycle. As shown schematically in Fig. 2. Zhang et al. [39] have proposed that narrow micropores act as micro-reactors to confine the electrochemical reactions within the micropores and prevent sulfur and lithium polysulfides from release into the electrolyte, which improves the reversible capacity.

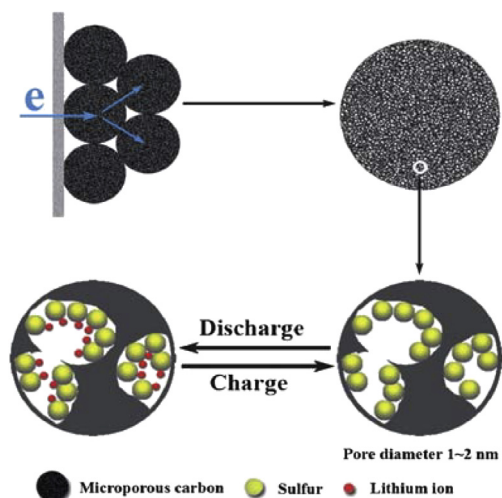


Fig. 2. A scheme of the constrained electrochemical reaction process inside the micropores of the sulfur-carbon sphere composite cathode. Reproduced from Ref. [39] with permission of Royal Society of Chemistry.

Also, they find that porous cathodes fully impregnated with sulfur have a reduced discharge capacity in comparison to those cathodes with less sulfur in micropores [40]. Their finding is consistent with other reports for mesoporous carbon-sulfur materials [41,42]. When pores are completely filled with sulfur, there are no channels for Li^+ migration and thus only limited electrochemical reactions can take place. Active carbon [40] and carbon derived from fish scales [43] have also been examined as microporous hosts with narrow pore structures for sulfur. The large surface area and many micropores for sulfur impregnation have made these carbon materials good cathodes with high ionic conductivity and capacity retention.

Given that cathodes made of cyclooctasulfur- S_8 would result in soluble polysulfide intermediates during cycling, employing different allotropes of sulfur to mitigate the capacity decay with little formation of polysulfides could be an effective strategy to prevent the loss of the sulfur content at the cathode. Xin et al. [44] have proposed a novel approach by using small sulfur allotropes S_{2-4} (S_2 , S_3 , and S_4) as the cathode active materials. These metastable sulfur molecules can completely avoid the transition between S_8 and S_4^{2-} when confined in microporous carbon with pore size of about 0.5 nm. This becomes possible because large S_{5-8} molecules cannot be stored in such small pores and thus cannot be formed in the cycling processes. As a result, porous cathodes made of small sulfur allotropes S_{2-4} (S_2 , S_3 , and S_4) exhibit improved capacity performance over the counterparts with S_8 as the cathode active material. Fujimori et al. [45] have recently created linear chains of sulfur displaying metallic behavior with conductivity that may be promising for Li-S battery applications. All of these studies suggest that controlling allotropes of sulfur could be an effective method to improve the electrochemical properties of the Li-S cell, and thus more attention should be paid to this area in the future.

Despite many advantages of microporous materials discussed above, micropores have confined spaces that can accommodate sulfur active materials, resulting in limited enhancement in the capacity. Therefore, pore volume needs to be increased to improve sulfur loading. For this reason, mesoporous materials (with pore size ranging from 2 to 50 nm) have also been studied extensively as hosts for sulfur [33]. In addition to the increased sulfur loading, mesoporous materials with increased pore sizes over micropores also allow easy access to sulfur by liquid electrolytes for facile Li^+ ion migration, thereby reducing voltage hysteresis, rendering long

battery cycles, and offering high capacity retention. Ji, Lee and Nazar [46] have reported highly ordered mesoporous carbon-sulfur electrodes exhibiting high pore volume, uniform pore diameters and interconnected porous structure by employing CMK-3, a well-known mesoporous material. Their results show that this cathode renders a highly enhanced performance with reversible capacities up to 1320 mAh g^{-1} .

In design of mesoporous cathodes, several critical factors that are essential for improving the performance of lithium-sulfur systems need to be considered. Li et al. [41] have investigated the effects of the pore size of mesoporous carbon. They have synthesized a series of mesoporous carbon with different pore sizes (22 nm, 12 nm, 7 nm, and 3 nm) and pore volume ranging from 1.3 to $4.8 \text{ cm}^3 \text{ g}^{-1}$. Their results indicate that the overall battery performances of the four electrodes are very similar if the mesopores are completely filled with sulfur. However, partial filling of sulfur leads to a better battery performance than complete filling of sulfur. These results reveal that increasing sulfur contents will not make a difference on capacity performance if the entire pore volumes are impregnated with sulfur. This phenomenon is likely related to the mechanism that full sulfur filling in mesopores hinders the access of electrolyte and ion transport. Through optimization of pore sizes and sulfur loading, the authors have achieved cathodes with initial capacity of $\sim 1400 \text{ mAh g}^{-1}$ and good cycling stability with capacity retention of $\sim 840 \text{ mAh g}^{-1}$ after 100 cycles. Chen et al. [47] and Tao et al. [42] have also studied the relationship between loaded sulfur with different pore sizes and battery performance, and obtained similar results.

Other efforts in studying of mesoporous cathodes include nitrogen doping and bimodal pore structure. The study of nitrogen-doped mesoporous carbon [48] reveals high efficiency immobilization of sulfur and better performance than that without nitrogen doping. The bimodal pore structure of mesoporous carbon, first reported by Liang et al. [38], have been studied recently by other researchers [49,50]. Generally speaking, the large pores are in favor of accommodating the liquid electrolyte where lithium ions have high conductivity, while the small ones can host sulfur and confine polysulfide species to prevent their outflow. He et al. [49] have synthesized high rate sulfur bimodal porous carbons as the cathode for lithium sulfur cells with evaporation-induced self-assembly approach rather than potassium hydroxide (KOH) treatment presented in other papers [38,51]. Through optimizing the ratios of carbon/silica/surfactant, the authors have obtained the desired bimodal distribution and demonstrated an initial capacity at 995 mAh g^{-1} and the capacity of 550 mAh g^{-1} after 100 cycles at 1 C rate. Besides, this work has also applied mesoporous silica, which is believed to increase hydrophilicity and help trap more polysulfides, to enhance the cycle stability.

Macroporous carbon as the cathode for the Li-S system has been less investigated as compared to microporous and mesoporous materials, due to its open structures which cannot effectively retain sulfur and intermediate polysulfides within pores. Wei et al. [52] have adopted KOH activation to obtain hierarchical porous structure including macropores. Despite a high initial capacity of 1265 mAh g^{-1} observed, the decay of the macroporous carbon-sulfur cathode is substantial since the capacity decreases to 643 mAh g^{-1} only after 50 cycles.

Given the tremendous potential of porous materials in Li-S battery applications, it will be highly beneficial if the kinetics associated to ion migration can be studied in more details. Further studies of a variety of techniques to construct optimized porous materials are equally important. Details including the theories and methods for synthesizing porous materials can be accessed with some reports [34,35,53] as we do not focus on these with a limited space in this review.

3.2. Two dimension sulfur-containing nanotubes/nanofibers

Carbon nanotubes and carbon nanofibers, as attractive matrices for sulfur, have attracted considerable attention [54–57]. The intimate contact between conductive nanotubes and sulfur can enable fast electron and lithium ion transport in electrodes [58]. In addition, flexible carbon nanotubes can accommodate the volume expansion of sulfur during cycling.

Ahn et al. [56] have prepared sulfur-containing multiwalled carbon nanotubes (MWCNTs) via a direct precipitation method for the cathode. In this study, sulfur is not trapped by or bonded strongly to nanotubes. As a result, the discharging capacity is very low upon 30 cycles. In contrast, Yuan et al. [59] have taken advantage of the capillary effect between the sulfur and MWCNTs to construct a novel electrode with carbon nanotube as the core. This composite shows a good cycle life compared to the counterpart made by simply mixing sulfur with MWCNTs [56]. However, a low initial capacity with only 650 mAh g^{-1} is observed, probably because sulfur is directly coated on the surface of the MWCNT host, resulting in the dissolution of polysulfide during charge/discharge processes. In order to tackle this dissolution issue, Zheng et al. [60] have utilized the anodic aluminum oxide (AAO) membrane template to obtain hollow carbon nanofibers, followed by infusing sulfur into the hollow fibers. Fig. 3 shows schematically the process on how the hollow carbon nanofibers with sulfur encapsulated inside are obtained. This cathode displays a capacity of more than 900 mAh g^{-1} after 30 cycles at 0.2 C, and has impressive capacity retention and coulombic efficiency up to 99% with the addition of LiNO_3 . Another binder free and flexible cathode comprising chemical vapor deposited carbon nanotubes filled with sulfur has also been fabricated by template methods [61]. This novel cathode delivers a capacity as high as 1438 mAh g^{-1} based on sulfur as the active materials. This cathode not only facilitates the transportation of electrons and ions, but also shortens the distance of lithium ions diffusion in electrodes, contributing to a fast kinetic reaction.

Polymer materials [62] have been proven as an effective matrix in housing and controlling the release of desired chemicals in drug

delivery area. Inspired by this thought, Xiao et al. [63] believe that simple physical confinement is not sufficient for trapping sulfur polysulfide and prohibiting its dissolution in electrolytes. They report a facile and environmentally benign process for synthesis of polyaniline nanotubes (PANI-NT) with encapsulated sulfur. Thanks to the strong physical bonds and chemical interactions among the polymer framework, sulfur and polysulfides, the cathode yields 837 mAh g^{-1} at 0.1 C in the 100th cycle, and 432 mAh g^{-1} at 1 C even over 500 cycles, corresponding to the coulombic efficiency of over 90%. Cui's group has also realized the effective function of polymers in interacting with sulfur and polysulfides, and investigated the modification of the interface between carbon nanotubes and sulfur using polyvinylpyrrolidone (PVP) [64]. They have also conducted theoretical calculation of the interaction between the lithium sulfide species and the carbon surface via first-principles calculations. Their results show that PVP can enhance the interaction of polysulfides with the carbon nanotubes, thereby minimizing the detachment of polysulfides from the carbon surface and improving the capacity retention. The cathode constructed using such PVP-modified sulfur-containing carbon nanotubes exhibits superior capacity retention of 80% over 300 cycles at the 0.5 C current rate.

3.3. Graphene–sulfur electrodes

Graphene as a two dimensional and one atom thick conductor possesses high conductivity, mechanical strength and flexible structure. Despite these advantages for the potential application in energy storage materials, it is not widely investigated as the host for sulfur in the cathode due to its sheet-like shape and open structure, causing active materials to readily diffuse out.

Nevertheless, some reports have demonstrated promising results [65,66]. Zhou et al. [66] have designed a unique sandwich structure placing elemental sulfur between two membranes made of graphene. One of them replaces the Al current collector to provide better contact with active materials for excellent conductivity while achieving much higher energy density. The other coated on the separator offers a strong barrier layer to prevent the diffusion of polysulfide intermediates to the anode, alleviating the shuttle problem. A similar structure reported recently employing reduced graphene oxide film between the cathode and the separator shows improved capacity performance as well [67].

Another way to mitigate the effect of open structure is to fabricate elaborate structures to confine sulfur while providing good ionic and electronic conductivities. Wang et al. [68] have engineered a cathode material by first coating sulfur particles with poly(ethylene glycol) (PEG) and then wrapping these coated particles with graphene oxide sheets decorated by carbon black nanoparticles (Fig. 4). In this elaborate structure, carbon black and graphene facilitate the transport of electrodes and ions, while PEG polymer and graphene serve to trap sulfur and its intermediate products. The cathode made of such elaborate structures has displayed a reversible capacity of $\sim 600 \text{ mAh g}^{-1}$ and less than 15% degradation after 100 cycles.

3.4. Three dimensional nanostructured sulfur composites

Three dimensional (3D) nanoarchitectures provide porosity for increased power by reducing the length of the diffusion path [58,69,70] and accommodate volume changes of active materials during cycling [71]. Also, porosity offers necessary pathway for electrolyte penetration, resulting in enhanced lithium ion diffusion and fast kinetic reactions [72]. Thus, considerable efforts have been devoted to the development of 3D sulfur electrodes in order to achieve high energy density and high rate capability Li–S batteries.

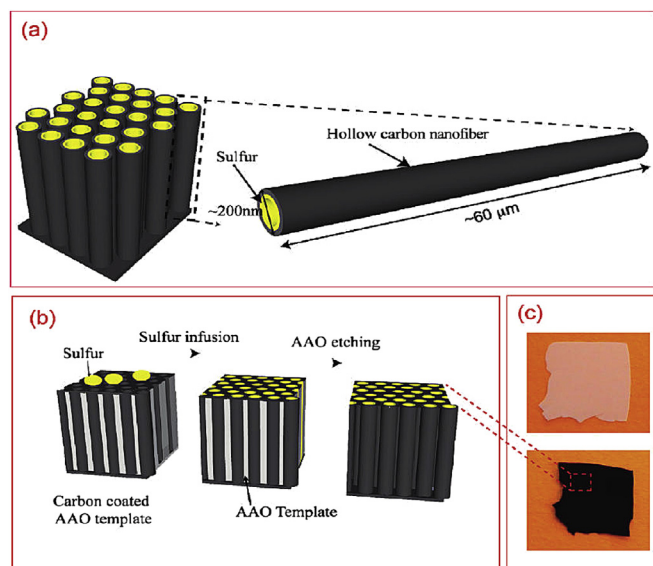


Fig. 3. Schematic of design and fabrication process of hollow carbon nanofiber/sulfur composite structure. (a) The design principle showing the high aspect ratio of the hollow carbon nanofibers for effective trapping of polysulfides, (b) the fabrication process of carbon/sulfur cathode structure, and (c) digital camera images showing the contrast of the AAO template before and after carbon coating and sulfur infusion. Reproduced from Ref. [58] with permission of American Chemical Society.

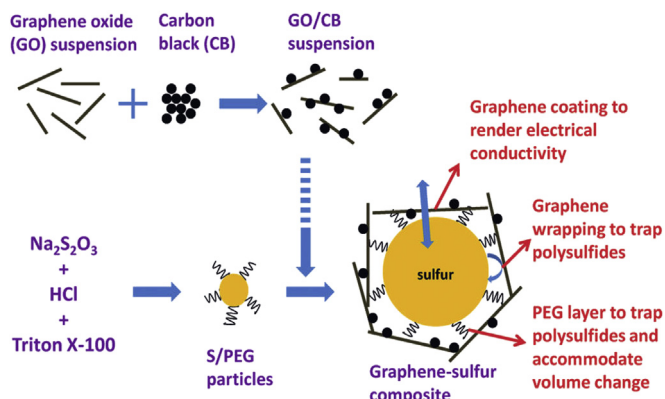


Fig. 4. Schematic of the synthesis steps for a graphene-sulfur composite, with a proposed schematic structure of the composite. Reproduced from Ref. [66] with permission of American Chemical Society.

Chen et al. [73] have developed 3D multi-walled carbon nanotubes to house sulfur or lithium sulfide, and achieved much enhanced capacity with 780 mAh g^{-1} remaining after 200 cycles at a current density of 0.5 A g^{-1} . Other researchers have obtained the increased capacity retention through engineering sulfur [59,74] or lithium sulfide [75] in 3D carbon nanotubes matrices. They believe that 3D carbon nanotube structures can buffer the stress caused by the volume expansion of sulfur upon discharging [73], and retard the out-diffusion of sulfur-based materials from electrodes [74]. Besides, the pores existing in such 3D structures can facilitate electron diffusion while allowing fast ions transport [75].

3D polymer nanotubes have been investigated as well. Compared to carbon nanotubes, polymer nanotubes [63,76] enable trapping of intermediate polysulfides effectively, rendering better battery performance. It is interesting to note that it usually gets marginal results by using two dimensional graphene to host sulfur active materials; however, with fabricating 3D unique graphene structures, Cao et al. [65] have obtained a high sulfur loading (70 wt %) and a reversible capacity of $\sim 505 \text{ mAh g}^{-1}$ at 1 C. In addition, embedding sulfur in 3D metal organic framework [77] as an alternative for the cathode has recently attracted the attention of researchers, due to the improved electrochemical performance it can have.

3.5. Core-shell and yolk-shell structures for sulfur cathodes

In order to effectively confine active materials, unique structures of the cathode to protect them from contacting electrolytes are required. In general, one-dimensional nanotubes/nanofibers and two-dimensional graphene are not sufficient to retard polysulfide dissolution due to their open end structures. Although open end structures are beneficial for the access of electrolytes and ion migration, these same structures also result in polysulfide leakage.

Core-shell structures have been explored to address the challenge of open end structures. In most core-shell structures, sulfur or sulfur-based compound acts as the core. Furthermore, high content of sulfur up to approximately 85% embedded in the shell can be achieved [78,79]. Broadly speaking, core-shell structures as a unique framework can be any dimensions based on the core. For instance, sulfur is encapsulated in carbon nanotubes as a core-shell structure [59,80]. In this review, however, we focus on the core-shell spherical structure.

Additionally, it is noted that the yolk-shell structure has also been investigated [81]. The difference between the yolk-shell structure and core-shell structure is that void space exists between

the core and the shell in the yolk-shell structure, which can be termed as core@void@shell. There are a lot of techniques to synthesize the core-shell and yolk-shell structures, most of which have been investigated in making electrodes for lithium ion batteries [35,82]. As mentioned above, the core material of the Li-S battery is sulfur or other sulfur based components, while the shell providing the protection against polysulfide dissolution is usually conductive materials to facilitate both ion and electron transport. In what follows, some examples of demonstrating the great potential of both core-shell and yolk-shell structures in sulfur cathodes are reviewed.

Although most of works focus on sulfur as the core material, some research has been done with sulfur as the shell [83]. In the latter case, capacity retention is poor [83]. However, not all the cathodes with sulfur as the core exhibit good capacity retention. For example, sulfur powders coated with conductive polymers or carbon are widely synthesized through chemical oxidative polymerization route [84,85], which is facile. However, the cathodes developed via this method usually do not display improved capacity retention. Two reasons may be responsible for this phenomenon: (1) insufficient coating with conductive materials results in polysulfide dissolution into electrolytes [85]; and (2) the volume expansion and constriction during electrochemical processes could lead to fracture of the shell structure, leading to the leakage and dissolution of polysulfides.

There are two general approaches that can be considered to address the aforementioned tricky problems. The first is to modify sulfur, e.g., using smaller sulfur allotrope [44] or ultrafine sulfur [86]. Chen et al. [86] have employed a novel membrane-assisted precipitation technique to obtain ultrafine sulfur with diameters ranging from 10 to 20 nm. After confining this superfine sulfur within the polymer shell, the authors have demonstrated an inspiring specific capacity (930 mAh g^{-1} after 50 cycles) although long cycling performance has not been reported yet.

The second general approach is to modify the core-shell framework by i) making double shells to increase the effectiveness of preventing polysulfide dissolution, ii) making soft shells to accommodate volumetric expansion in discharge, iii) introducing hollow space between the core and shell to make the yolk-shell structure, or iv) a combination of these methods. Along these directions, confining sulfur in hollow double shells has recently been reported [87,88]. With void space between the core and double shells, the volume expansion can be buffered. The double shell structure facilitates ion and electron transport as well [87,88]. Yolk-shell structures with empty space between the core and shell are very promising in solving the volumetric expansion problem [81]. Cui and coworkers [16] have recently explored the yolk-shell structure with sulfur encapsulated in the TiO_2 shell. Their synthesis procedure is schematically shown in Fig. 5. Monodispersed sulfur nanoparticles are first prepared via the reaction between sodium thiosulfate and hydrochloric acid. The sulfur particles are then coated with TiO_2 through controlled hydrolysis of titanium diisopropoxide bis(acetylacetonate). To engineer the yolk-shell nano-architecture, toluene is used to dissolve partial sulfur in the core, thereby generating empty space between the core and shell. This

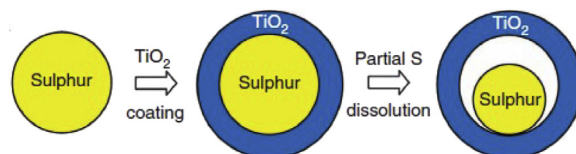


Fig. 5. Schematic of the synthetic process for the yolk-shell sulfur- TiO_2 . Reproduced from Ref. [15] with permission of Nature Publishing Group.

cathode exhibits a prolonged cycling performance over 1000 cycles with the average coulombic efficiency of 98.4% [16]. The favorable factors for the excellent results include the empty space in nanostructures to accommodate volume expansion, the intact TiO_2 shell with mesopores, and hydrophilic $\text{Ti}-\text{O}$ groups to bind with polysulfide anions, all of which are beneficial for minimizing polysulfide dissolution.

3.6. Polymer–sulfur nanocomposites

Polymer plays a vital role not only in the performance of electrolytes within lithium sulfur batteries, but also cathodes synthesis. Polymers, especially conductive ones, can be tailored or used to modify the surface of cathodes, facilitating ion and charge transport [64]. Also, polymers can adsorb polysulfides and retard their dissolution into electrolytes [89]. Ji and coworkers [46] have employed porous carbon as the host for sulfur, and used polymer modification as a chemical gradient to achieve improved electrochemical performance, although detailed data including extended cycle life and rate capabilities have not been published yet. Fu et al. [90] have developed polypyrrole–sulfur composite with the core–shell structure. The cathode made of such a composite yields a high initial capacity of $\sim 1050 \text{ mAh g}^{-1}$, and exhibits $\sim 200 \text{ mAh g}^{-1}$ higher capacity than pristine sulfur electrode upon 50 cycles at 0.5 C. Despite this advantage, it only has 67% capacity retention after 50 cycles. Similar results can be found in other reports with the same engineered composition and structures [84,89,91,92].

The studies in polymer–sulfur composites have revealed two general approaches that can enhance the electrochemical performance of polymer–sulfur composites. First, the sulfur size should be small (in nanometers). Through melt infiltration of sulfur to the pores of poly(pyrrole-co-aniline) (PPyA) copolymer nanofibers, Qiu et al. [76] have prepared nanosized sulfur in polymers, and obtained a higher initial capacity and less fading than those obtained by Fu et al. [90] and many others [84,89,91,92]. Yang et al. [93] have also improved the performance of lithium sulfur batteries by melting sulfur into CMK-3 mesoporous carbon to form confined sulfur with 2–50 nm in size and using a conductive polymer as the coating to prevent polysulfide dissolution.

The second general approach is based on the belief that simple physical confinement with polymer modification or function on the electrode surface is not sufficient for retarding polysulfide dissolution and thus not effective in achieving a long cycle life. In order to achieve better trapping of intermediate products by polymers and thus superior cycling life, Xiao and coworkers [63] have proposed a facile and environmental friendly synthesis process with self-assembling polyaniline nanotubes (PANI-NT) for sulfur encapsulation. The polymer treated with sulfur at 280°C forms cross-linked, three dimensional and structurally stable polyaniline nanotube-sulfur composites (SPANI-NT/S), as shown in Fig. 6. This polymer framework offers strong physical and chemical confinement to sulfur-based components, alleviating the loss of active materials greatly. Additionally, the soft polymer matrix and nanostructured sulfur components have provided cushioning for volume changes during electrochemical reactions.

Recently, Cui and colleagues [12] have further modified polymer–sulfur nanocomposites by introducing empty space between the sulfur core and encapsulating polymer. Fig. 7 presents schematically the formation of their PVP-encapsulated hollow S nanospheres [12]. In aqueous solution, PVP molecules can self-assemble to form a double-layer structure, with hydrophobic alkyl backbones as the interior wall and hydrophilic amide group as the exterior wall, leading to perfect growth of S nanospheres within the hydrophobic interior due to the hydrophobic nature of

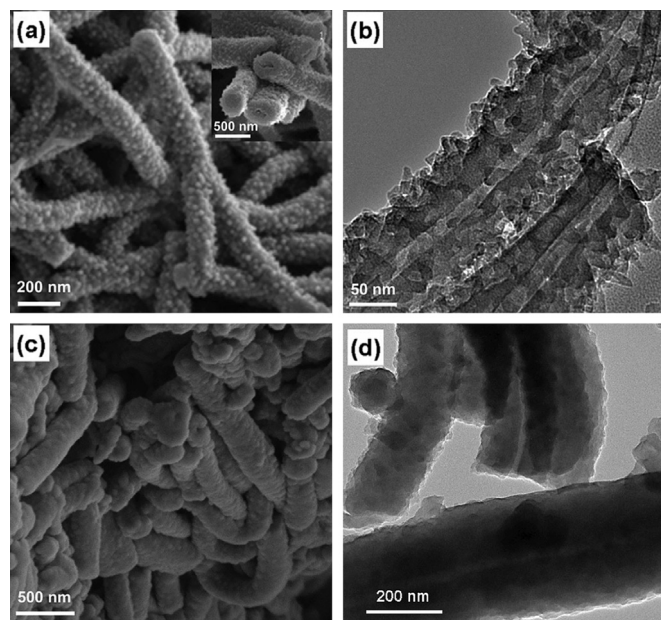


Fig. 6. SEM (a) and TEM (b) images of the neat PANI-NT. SEM (c) and TEM (d) images of the SPANI-NT/S composite. Reproduced from Ref. [61] with permission of John Wiley & Sons, Inc.

S. Herein, PVP not only functions as a soft template for the formation of S nanospheres with a unique hollow structure, but also serve as a reservoir to confine sulfur and polysulfides via strong interactions. The monodispersed and polymer-encapsulated hollow sulfur cathode displays excellent cycling properties to 1000 cycles and great capacity retention of 73.4% at 0.5 C after 500 cycles [12].

Another effective way to further enhance the functionalities of polymers in the sulfur cathode is to engineer polymers with self-healing properties. Self-healing polymers applied in electrodes include two main categories, one of which is soft polymers with dynamic bonds [94] to replace binders, offering flexible buffer for volume changes; the other one is self-healing polymers stored within micron-sized capsules [95]. If there exists damage or cracking within electrodes, the capsules will break and thus the embedded polymer agent will leak out to heal the fractures. However, such a healing concept through the encapsulated polymer agent remains to be studied experimentally [94]. Based on these thoughts, we believe that design and utilizing of polymer materials can be an alternative and impactful approach to address the polysulfide dissolution and volume change problems present in Li–S battery systems.

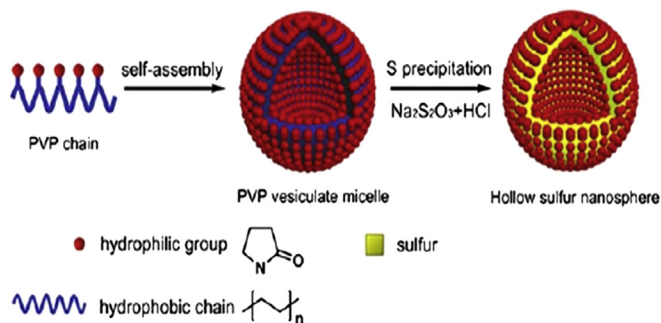


Fig. 7. Formation mechanism of PVP-encapsulated hollow S nanospheres. Reproduced from Ref. [16] with permission of National Academy of Sciences.

3.7. Li_2S cathodes

Lithium sulfide (Li_2S), the final discharge product of sulfur element, has attracted much attention lately [96–101] as a promising cathode material for high energy Li–S battery systems due to its high theoretic capacity of 1166 mAh g^{-1} [102], nearly 1 order of magnitude higher than traditional metal oxides/phosphates cathodes. Moreover, compared to the sulfur cathode, Li_2S is a pre-lithiated cathode and does not require lithium metal as the anode, mitigating safety concerns caused by lithium metal and its dendrites. Li_2S can be paired with other promising anodes, such as silicon [102] and tin [103]. As the cathode is assembled in the discharge state of sulfur electrodes, an essential activation potential about 1 V is required [104] to convert Li_2S to lithium, sulfur and other intermediate products, such as Li_2S_x ($2 \leq x \leq 8$).

A big challenge remaining for this cathode is the slow kinetics and low rate capability as a result of the poor electronic and ionic conductivities of Li_2S . The high dissolution of polysulfides is also a concern for Li_2S cathodes. Although ball-milled Li_2S with carbon black has been utilized directly as the cathode [75,103], carbon coated [104] or porous materials filled [102] lithium sulfide is usually applied to increase the conductivity and sequester polysulfides from electrolytes to avoid or minimize polysulfide dissolution.

Lately, dispersing lithium sulfide uniformly in a carbon host has been realized through exploiting strong interactions between lithium ions and nitrile groups of polyacrylonitrile (PAN), followed by carbonization of the cross-link polymer with heat treatment [105,106]. This $\text{Li}_2\text{S}/\text{C}$ cathode has delivered a reversible capacity of around 900 mAh g^{-1} based on the active material mass upon 20 cycles, which approaches the theoretical capacity (1166 mAh g^{-1}). Lin and coworkers [107] have fabricated the Li_2S – Li_3PS_4 core–shell structure via the reaction of nanosized Li_2S with P_2S_5 in tetrahydrofuran (THF) to form the Li_3PS_4 shell, a superionic conductive material. They have tested the cell in solid electrolytes to eliminate the polysulfide shuttle and obtained good capacity. Zheng et al. [108] have advanced a novel approach to prepare a very stable $\text{Li}_2\text{S}/\text{microporous carbon (MC)}$ cathode by first vaporizing small sulfur molecular into MC, and subsequently pre-lithiating S/MC with the assistant of spraying stabilized lithium metal powder, a novel and facile *in situ* strategy. The capacity retention of this cathode remains 650 mAh g^{-1} after 900 cycles, which is the best result reported to date for Li_2S electrodes, despite the low current density (0.1 C) applied in this work.

3.8. Summary of sulfur-based cathodes

There are three major problems associated with sulfur cathodes: (1) the insulating nature of sulfur and lithium sulfide materials; (2) the high dissolution of polysulfides in organic electrolytes; and (3) volume change of the active materials during lithiation and delithiation processes.

Porous materials, especially microporous and mesoporous materials with high electronic conductivity are promising for hosting sulfur. These porous materials divide sulfur into nanoscales and offer pathways for electrolytes, both of which are favorable for shortening the ion diffusion length and making electrolytes readily available, thereby enhancing reaction kinetics within the cathode. The open ends of nanotubes/fibers and the non-closure nature of graphene limit their applications in sulfur-based cathodes unless special structures, i.e., closed architectures, can be fabricated or strong interactions between them and polysulfides can be achieved. Compared to the open end framework, core–shell and yolk–shell structures are inspiring for housing sulfur and alleviating polysulfide dissolution.

Polymers as widely employed materials to retard polysulfide dissolution in electrolytes play a vital role in sulfur cathodes. They can be cross-linked with sulfur or coated onto the sulfur surface. Alternatively, self-healing polymers can be used to address the challenge of volume expansion and fracture of sulfur cathodes. More research in self-healing polymers is warranted as these materials have the potential to be the next-generation materials for the cathode of Li–S batteries.

Lithium sulfide is also promising as the cathode of Li–S cells because it can be paired with metal free and other high energy anodes, e.g., silicon and tin. However, more efforts are required to better address the insulating properties and prevent polysulfide dissolution. Integrating several strategies discussed above to fabricate sulfur-based cathodes is another way to solve cathode issues encountered in the Li–S battery.

4. Selection of anodes, electrolytes and separators

As discussed above, one of the barriers that hinder the practical development of Li–S cells is the polysulfide dissolution in electrolytes, which leads to shuttle behavior and further corrodes lithium metal anodes. This challenge is not related to the cathode only; it is affected by the properties of anodes and electrolytes, and may be overcome by controlling and engineering the anode and electrolytes along with electrolyte additives, binders and separators. However, these components are little mentioned [13,18–22,109] or partially discussed [24] in earlier review articles. As will be shown later, electrolyte additives, binders and separators also play vital roles in Li–S batteries. Thus, review of the progress in these components will be presented in the following sections. To settle the challenges of the Li–S system as a whole and pave the way for future investigation, conclusions and optimizations in controlling and engineering the anode, electrolytes, electrolyte additives, binders and separators are absolutely necessary.

4.1. Anode

Lithium metal, possessing the highest gravimetric energy density of all anode materials, is generally the anode material for typical lithium sulfur batteries. It can provide the maximum cell voltage when coupled with the cathode, as compared with other anode materials. However, it is very reactive in common electrolyte media, and redox reactions between organics/polysulfides and metal readily occur on the electrode surface, thus forming a passivating layer [110] and the shuttle phenomenon. Furthermore, lithium dendrites can form and penetrate through the separator, shorting the cell and causing thermal runaway and fire at last.

To mitigate or circumvent the safety issue, protection layer to the surface of lithium anode was introduced [111] and lithiated cathodes were considered, such as lithiated silicon [112]. Nevertheless, the capacity decay is too fast during electrochemical cycles and the voltage of these as-assembled cell ranges from 1.5 V to 2 V. At present, using metal-free anode is widely paired with Li_2S cathodes, which is much controllable compared to the fabrication of pre-lithiated anodes, while yielding a theoretical specific energy of 1550 Wh kg^{-1} [102].

4.2. Electrolytes for Li–S batteries

Considerable efforts to solve polysulfide dissolution and the shuttle phenomenon have been paid to electrolyte studies. Developing new electrolytes and additives is extremely desirable for realizing good interfacial architectures and great properties of Li–S batteries.

4.2.1. Liquid organic electrolytes

Liquid organic electrolytes contain lithium salts and organic solvents. Solvents are considered very important although the significance of lithium salts is also reported for improving the battery performance [112]. Properties for electrolytes applicable in Li–S batteries include: (1) good polysulfide solubility [113], which is favorable for the reactions between lithium and sulfur-based compounds and utilization of active materials [27]; (2) chemically stable with polysulfide species (anions and anionic radicals) and Li anode; and (3) low viscosity for fast ion and charge transports.

Based on the requirements above, conventional carbonate solvents in lithium ion batteries are usually not suitable for Li–S cells due to their chemical reactivity with polysulfides [114–116]. Therefore, alternative ether solvents and poly(ethylene glycol) (PEO) [117,118] have to be considered. It is found that cyclic and linear ethers, including tetrahydrofuran (THF) [119], 1,3-dioxolane (DOL) [120], 1,2-dimethoxyethane (DME) [121], and tetra(ethylene glycol) dimethyl ether (TEGDME) [120], are suitable electrolytes due to their high polysulfide dissolution. Especially, TEGDME is very promising because high capacity over 1200 mAh g⁻¹ has been achieved [29,120]. Chang et al. [113] have investigated the battery performance with combination of TEGDME and DOL using LiCF₃SO₃ as the salt. After optimization of their ratios, this electrolyte mixture displays better ion conductivity than a single solvent with salts.

Gao et al. [114] have studied seven solvents with common salts and found that TEGDME and DOL/DME are attractive solvents. The benign compatibility of DOL/DME with lithium metal and their good polysulfide solubility have also been reported by Yang et al. [104]. Very recently, electrolytes containing CF₂HCF₂OCH₂CF₂CF₂H (D2) to blend with DOL solvent as a substitute for linear DME have been demonstrated to possess favorable performance [122]. It is probably that D2 forms a surface film on the lithium metal, impeding polysulfide anions reduction and thus alleviating the redox shuttle [122].

4.2.2. Solid state electrolytes

The shuttle phenomenon is inevitable when liquid electrolytes are employed in Li–S systems due to polysulfide dissolution and reduction on the anode surface. In order to fundamentally eliminate the existence of polysulfide ions, solid electrolytes as an alternative approach have attracted intensive attention widely. The requirements of solid electrolytes for Li–S batteries include: (1) good conductivity for lithium ions; (2) being stable with lithium metal anodes; and (3) high contact area between electrodes and electrolytes. The main hurdle for the practical application of solid electrolytes is their low ionic conductivity [123–125]. However, with the emergence of solid media possessing lithium ion conductivity comparable to that of liquid electrolytes [126], all-solid-state electrolyte cells could become the next-generation batteries.

Since the ion migration rate is a challenge for all-solid-state Li–S cells, PEO with lithium salts containing finely dispersed nano-sized ZrO₂ particles [127] or LiAlO₂ filler [128] has been developed. The capacity closed to theoretical and high coulombic efficiency are achieved at elevated temperatures (90 °C), and a stable anode interface is obtained, likely due to the dispersed ceramic filler as an interfacial stabilizer [127]. Also, various other solid electrolytes, such as Li₂S–SiS₂ powers [129], thio-LiSICONs (lithium super-ionic conductor) [130], and Li₂S–P₂S₅ glass–ceramics [131–133], have been investigated. To increase the contact area with Li₂S–P₂S₅ glass–ceramics electrolytes, cathode materials consisting of sulfur and CuS have been synthesized via mechanical milling [131] to reduce the particle size. In addition, sulfur cathodes with Li₂S–P₂S₅ glass–ceramics electrolytes would suffer from low sulfur content because the electrochemical reaction in solid state media appears

to be point-to-point reactions and lots of conductive materials are needed for facilitating lithiation/delithiation processes. Hence, the construction of a favorable interface among sulfur, small amounts of conductive additives and electrolyte materials is desired to increase the sulfur content of electrodes. Nagao et al. [134] have recently increased sulfur contents through mechanical milling of the sulfur and nanosized carbon mixture at high temperatures at which sulfur becomes liquid with a very low viscosity and thus can readily form a liquid–solid (molten sulfur–nanocarbon) interface. Liu et al. [135] have first reported sulfur-rich compounds with high ionic conductivities. Upon utilizing them to lithium sulfide cathodes and electrolytes, excellent electrochemical reversibility during battery cycling has been obtained [136].

4.2.3. Gel polymer electrolytes

Gel polymer electrolytes (GPE) comprise solid matrices providing mechanical strength and liquid electrolytes responsible for electrochemical properties. Theoretically, they contain advantages of solid electrolytes impermeable to polysulfides and suppressing dendrite formation and advantages of liquid electrolytes with good conductivity.

The preparation procedure of GPE generally includes three steps: (1) synthesis of the polymer matrix; (2) casting or hot-pressing of the polymer matrix to form membranes; and (3) soaking the membrane with liquid electrolytes and lithium salts. Hassoun and Scrosati [98,103] have employed PEO/LiCF₃SO₃, EC/DMC and LiPF₆ as the matrix, liquid solution and lithium salts, respectively, to fabricate GPE for Li–S batteries. Their results show that the interfacial resistance is still high and good capacity retention is not achieved. These results are likely due to the poor liquid electrolyte retention in the GPE [137], thereby leading to fast fading of conductivity.

A favorable alternative to have high retention of the liquid electrolyte in the GPE is to use electrospun nanofibrous membranes based on different polymers [138–142]. These GPE not only have high interfacial compatibility, wide oxidation stability and excellent ionic conductivity, but also possess high liquid electrolyte uptake and serve as a good host due to fully interconnected pore structure of polymer membranes [140]. Also, results with the GPE tested in lithium ion batteries are promising [140–142].

Another choice is tris(methoxypolyethyleneglycol)-borate ester (PEG-B) that can increase ionic conductivity and Li-ion transference number [143,144]. Jin et al. [145] have explored PEG-B as plasticizers for the GPE to get low interfacial resistance and alleviate the migration of polysulfide anions. Another approach to enhance the ionic conductivity and maintain the liquid electrolyte within GPE is to use functional groups to bond with the liquid electrolyte. Along this line, Jeddi and coworkers [146] have fabricated functionalized poly(methyl methacrylate) (PMMA) containing trimethoxysilane domains and blended them with PVDF-HFP to form a GPE. Li–S cells with this GPE have delivered higher ionic conductivity compared to that of GPE without functionalized groups, and displayed little capacity decay.

4.2.4. Ionic liquid electrolytes

In addition to the three types of electrolytes discussed above, ionic liquid (IL) electrolytes have also attracted much interest. Ionic liquids are defined as liquid comprising entirely ions. Thus, they are different from organic electrolyte solutions. They have a variety of merits, including negligible vapor pressure, non-flammability, high lithium ion conductivity, wide electrochemical window [147], and the ability to inhibit the formation of lithium dendrites [148–150].

Yuan et al. [14] have demonstrated that sulfur cathodes exhibit greatly improved performance in an IL electrolyte composed of n-

methyl-*n*-butyl-piperidinium bis(trifluoromethanesulfonyl) imide (PP14TFSI). The improvement can be contributed to the suppressed dissolution of polysulfides in the electrolyte. Other ILs, such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMITFSI) [151] and *n*-methyl-*n*-allylpyrrolidinium bis(trifluoromethanesulfonyl) imide (PIA3TFSI) [152], have also been investigated as the electrolytes for Li–S cells, and exhibited superior capacity performance. Watanabe and coworkers [153] have compared the electrochemical capabilities of two different solvents, *N,N*-diethyl-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide ([DEME][TFSI]) and TEGDME. The former is an IL, while the latter is an organic solvent. Their results show a very suppressed solubility of Li_2S_m ($2 \leq m \leq 8$) in the IL, whereas the dissolution and precipitation of Li_2S_m take place in the organic electrolyte. Furthermore, their results indicate that conventional organic solvents such as TEGDME have high donor ability, while the IL has low donor ability owing to the weak Lewis basicity of [TFSI][−] anion, favorable for significantly suppressing Li_2S_m dissolution and immobilizing Li_2S_m on the electrode [153].

However, considering the viscosity and high price of ILs, it is not cost-effective to totally employ ILs as the solvents of electrolytes. Thus, many researchers [115,154–156] have focused on the addition of ILs to the organic electrolytes to attain superior properties. Ma et al. [155] have adjusted the viscosity and conductivity of electrolytes with different contents of PYR14TFSI, and shown that the shuttle mechanism is greatly inhibited and the coulombic efficiency over 98% upon 100 cycles can be obtained when the content of PYR14TFSI is 50 vol.%. Similar results have been acquired in other studies [115,157]. Moreover, based on their work, Shin and Cairns [157] have believed that the PYR14TFSI + LiTFSI + PEGDME mixture is a very promising electrolyte for Li–S cells.

It is interesting to note that the solid electrolyte interface (SEI) exhibits a very different morphology when ionic liquids are used as electrolytes under the conditions with or without polysulfides [158,159]. More importantly, the SEI containing more sulfide-related species in the top layer has lower resistance and activation energy compared to those without ionic liquids, and exhibits more stable properties against the corrosion of polysulfides.

4.2.5. Electrolyte additives

In previous research work, additives always act a crucial role in advancing the battery behavior. Various electrolyte additives, such as LiNO_3 [32,160,161], toluene [162], dimethyl methyl phosphonate [163] and phosphorous pentasulfide [164] have been explored to enhance the cycle stability.

LiNO_3 has been widely applied as the additive in electrolytes [60,165], which is believed to enable the formation of protective film on the surface of the lithium anode, and favorable for high capacity retention. Zhang [32] has studied its effect on the lithium metal anode and the sulfur cathode. It is shown that the insoluble reduction products of LiNO_3 on the cathode affect the redox reversibility of the sulfur cathode adversely, although the passivation layer formed on the anode surface can suppress the redox shuttle of lithium polysulfides thanks to LiNO_3 . Furthermore, his work has demonstrated that the adverse effect can be avoided when the discharge cutoff voltage is raised to above 1.6 V [32].

It is very interesting to mention that some researchers have added lithium polysulfides to electrolytes [166,167]. Due to the presence of polysulfides anions, the dissolution of these ions is reduced and shuttle effects can be suppressed quite well. However, it needs to point out that when the content of lithium polysulfide is high in electrolytes, the viscosity may become so large that the ionic conductivity decreases.

5. Additives and other components

We believe that each component in Li–S systems plays a significant role in the battery performance. Accordingly, it is indispensable to discuss advances of other components developed to date.

5.1. Additives in cathodes

Note that additives are not only used in electrolytes as discussed in Section 4.2.5, but also utilized in cathodes for Li–S batteries. Therefore, it is imperative to present the effect of additives in cathodes on battery performance.

The functions of additives in cathodes mainly contain: (1) to increase the ionic and electronic conductivity, and (2) to adsorb intermediate polysulfides to mitigate its dissolution and shuttle phenomenon. For example, Nazar and coworkers have explored porous silica [168] and titania [169] as polysulfide reservoirs to host the carbon–sulfur composite. They have found that the hydrophilic pores of these inorganic materials adsorb hydrophilic lithium polysulfides reversibly and release them near the end of discharge process. The mesoporous silica and titania contribute to the stabilized cycling with high coulombic efficiency.

Song et al. [170] have exploited nanosized $\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}$, which has an adsorbing capability and the catalytic effect of dissociating chemical bonds, to inhibit polysulfide dissolution into electrolytes while promoting the redox reactions. This material has also been studied in combination with polyacrylonitrile (PAN) as sulfur cathode additives [171]. The S/PAN/ $\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}$ composite cathode has displayed good rate capability and a coulombic efficiency of about 100% over 100 cycles at 0.1 C. These results are very positive, showing that organic materials also have tremendous potential in trapping polysulfide anions. Fu and Manthiram [172] have mixed polypyrrole (PPy)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA), which is an ionic–electronic conductor, with sulfur to fabricate the cathode. The electrode with this organic mixture has exhibited discharge capacity as high as 500 mAh g^{-1} at 1 C after 50 cycles and excellent cycling stability due to the improved conductivity.

5.2. Membrane as the separator

The membrane in batteries functions as ions' conductor and electrons' insulator. Otherwise, electrons passing through the separator will cause internal short circuit. In addition, the mechanical strength and flexible ability are essential to protect it from being pierced and losing functions.

For lithium sulfur batteries the separator has been ameliorated to hinder migration of polysulfides to the anode side and thus prevent the shuttling. Nafion is known for its excellent stability and high cationic conductivity and widely used in the proton exchange membrane fuel cells [173–175]. More importantly, Nafion is a commercial product utilized as cation selective material with the ability to inhibit the polysulfide anions from transporting through [176]. Based on these capabilities, lithiated Nafion ionomer [176] and Nafion-coated polypropylene [177] have been investigated as separators and functional barriers for Li–S cells to improve the cycle performance.

Lately, Huang et al. [178] have developed an ion selective membrane by coating Celgard 2400 (a commercial membrane) with the Nafion solution. The SO_3^- groups-coated channels in this membrane allow positive-charged ions to pass through but reject hopping of negative ions (i.e., polysulfide anions) owing to the coulombic interactions. As demonstrated in Fig. 8, polysulfide anions are limited to the cathode side by the ion selective membrane, whereas lithium cations can shuttle between the two sides. A super

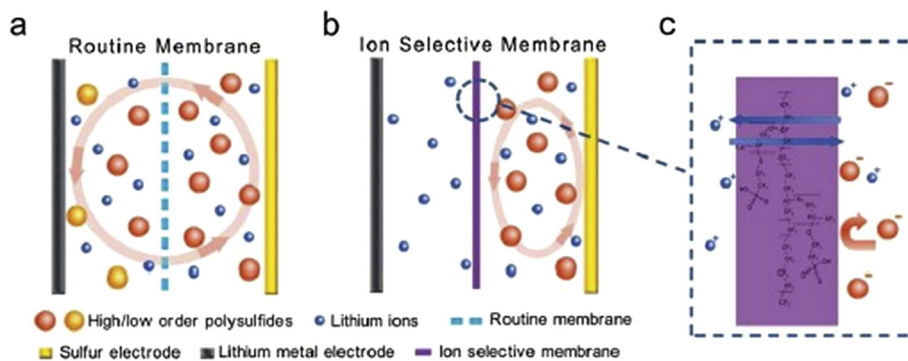


Fig. 8. Schematic of the different lithium–sulfur battery configurations. (a) Cells with routine membranes, in which polysulfides shuttle between the cathode and anode sides. (b) Cells with ion selective membranes, in which the polysulfide anions are limited to the cathode side. (c) Enlarged schematic showing that the cation permselective membrane allows the transport of lithium cations and blocks the polysulfide anions. Reproduced from Ref. [178] with permission of Royal Society of Chemistry.

low degradation rate of 0.08% per cycle is achieved in the initial 500 cycles with the assistance of ion selective membranes [178,179].

5.3. Binders

It is found that sulfur cathodes experience volume expansion when discharging and contraction when charging [66]. Therefore, it is crucial to control the morphology to maintain the stable structure of active materials and the carbon matrix. The role of binders is undoubtedly vital in a lithium sulfur cell, similar to that in lithium ion batteries [180].

The traditional functions of binders are to bond and keep sulfur-based active materials within the electrode, enhance the electric contact of sulfur with carbon, and link active materials with current collectors. However, binders with only these properties are not sufficient for a good cathode. Ideal binders for Li–S systems should contain additional features, including (1) being an effective dispersion agent to distribute sulfur-based particles and carbon uniformly; (2) low cost and low electric resistance; (3) possessing the capability of buffering the volume change of the sulfur-containing species; and (4) retaining polysulfides and limit its dissolution.

The most commonly used binder is poly(vinylidene fluoride) (PVDF) in virtue of its high electrochemical stability and great adhesive property. However, it can only be dissolved in some organic solvents, e.g., *N*-methyl-2-pyrrolidone (NMP), at elevated temperature above 80 °C. Under such conditions, sulfur sublimates and thus it leads to the loss of active materials. Thus, many other materials, such as poly(vinylpyrrolidone) (PVP) [181], carbonyl- β -cyclodextrin [182], Nafion [183], gelatin [184–186], PVP/poly(ethyleneimine) (PEI) [187] and styrene butadiene rubber (SBR)/sodium carboxyl methyl cellulose (CMC) [188], have been explored as binders to achieve more than one function. Results show that in addition to connect electrode composites, both of PVP/PEI and gelatin act as an effective dispersion agent to suppress the agglomeration of sulfur and carbon. SBR/CMC binders also favor a uniform distribution and provide a conductive network. Therefore, these binders are more functional than the common binders (PVDF and PEO).

Despite the progress described above, developing ideal binders to advance the performance of Li–S batteries still deserves more attention. We believe that the binder in the future should be related to self-healing materials, which can help to maintain a very stable structure of electrodes to guarantee a long cell cycle life.

5.4. Current collectors

The current collector is not just a substrate to increase the conductivity for electrodes; a good design of it enables favorable

control of lithium dendrites even when the cell is cycled at high current density [189]. Chung and Manthiram [190] have employed nano-cellular carbon (NC) as the current collector for sulfur cathodes. The nano-foam plate within this carbon serves as a reservoir to store active materials and localize the dissolved polysulfides. As a result, the current collector offers an excellently high discharge capacity and superior cycle stability. They have also explored the carbonized eggshell membrane (CEM) acting as the current collector [191]. The CEM works very similarly to NC functioning as a container of active materials and hosting the dissolved intermediates owing to its abundant pores, thereby stabilizing the electrochemical reaction in the cathode.

6. Novel components

Novel components are created with a goal to address challenges in the state-of-the-art Li–S technologies. The biggest hurdle is the dissolution of polysulfides, causing a lot of tricky problems, such as the loss of active materials, the shuttle phenomenon, corrosion of anodes, and the deposited lithium sulfide dendrites leading to the insulating of anodes and cathodes.

As shown in Fig. 9, Manthiram and his coworkers [192] have innovatively proposed to add an interlayer between the sulfur cathode and the separator for effectively retaining sulfur-based materials within the cathode side, thereby achieving stable cycle stability and high percentage utilization of active materials. The interlayer composites investigated include a treated carbon paper with hydroxyl functional groups and micro-cracks [192], multi-walled carbon nanotubes [193], meso/microporous carbon [194]

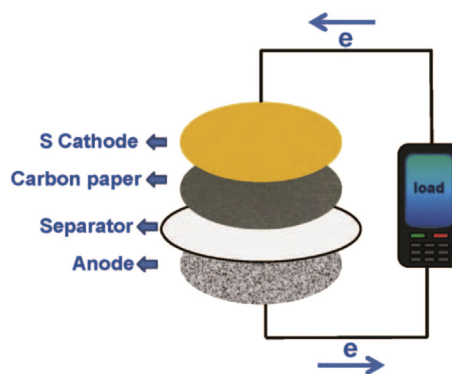


Fig. 9. Configuration of a lithium–sulfur cell with the treated carbon paper interlayer between the sulfur cathode and the separator. Reproduced from Ref. [192] with permission of Royal Society of Chemistry.

and carbonized eggshell membrane [191]. In addition, Han et al. [195] have adopted atomic layer deposited Al_2O_3 and assembled it at the same site as Manthiram and his coworkers [192] have done. With the interlayer, the cell has delivered an improved performance over those without the interlayer.

During the writing of this review article, a new hybrid anode for Li–S batteries was reported [196]. In this new hybrid anode, a protective shield made of graphite is added to the surface of the Li anode. This graphite layer (Fig. 10) in front of the Li metal functions as a self-regulated SEI layer to actively control the electrochemical reactions and minimize the deleterious sulfur side reactions. Li–S cells using such a hybrid anode exhibit capacities of $>800 \text{ mAh g}^{-1}$ for 400 cycles at a high rate of 1737 mAh g^{-1} [196].

7. Summary and future directions

This comprehensive review has systematically discussed nearly all of the recent advances in the lithium sulfur battery, which is one of the most promising candidates for energy storage due to its high theoretical specific capacity of 1672 mAh g^{-1} and energy density of 2500 Wh kg^{-1} , assuming the complete reaction of lithium and sulfur to the final product Li_2S .

Most efforts in Li–S cells have been devoted to the cathode study with a goal to increase the ionic and electronic conductivity and trap polysulfides within the electrode. Porous materials with micropores and mesopores have proved to have huge potentials for realizing the goal. Other nanostructured materials fabricated as sulfur cathodes possessing core/yolk shell frameworks and closed architectures have also attracted much interest. Li_2S and polymer materials for the applications in the cathode have the potential to address the issue of the lithium dendrites and retain intermediate products, respectively. The nanosized and special nanostructured

cathode materials with high active material content to effectively host polysulfides are going to be the subject of intensive research in the future.

Another main subject is surely electrolyte materials to address the challenges remaining in Li–S battery systems. Organic liquid electrolytes have the nature to dissolve polysulfides, leading to loss of active materials, while other electrolytes, i.e., solid and gel polymer electrolytes, have low conductivity although lithium dendrites and polysulfides dissolution can be superbly suppressed. To date, the very inspiring performance is achieved by the addition of ionic liquid to organic liquid electrolytes, which have high conductivity and little solubility for the intermediates. The future work in the electrolyte area for Li–S cells should focus on inhibiting the dissolution of polysulfides in electrolytes while optimizing their ionic and charge conductivity without compromising properties during prolonged electrochemical cycles.

Other components, if not more important, are much the same as cathodes and electrolytes. Based on the detailed presentation of each section in this review, the protection and additives are extraordinarily favorable for avoiding the formation of lithium dendrites and long cycling stability due to the protected lithium anodes. Other kinds of additives in cathodes and modified separators can be beneficial in retaining polysulfides within the cathode side, which leads to high utilization of active materials and promotes a long cycling life. Furthermore, good designs of binders, current collectors and interlayers not only facilitate ion and electron transports, but also enable the retention of polysulfides in pores or special structures as the reservoirs. These components deserve more attention due to their capabilities to address the main challenges of Li–S systems.

Despite enormous developments accomplished in the Li–S battery, the commercialization of this battery still has a long way to go, relying on technological breakthroughs in solving the three key problems defined in Section 2.2. We hope our comprehensive review can pave the avenues and inspire more work in these critical areas to facilitate the practical applications of this high energy storage system.

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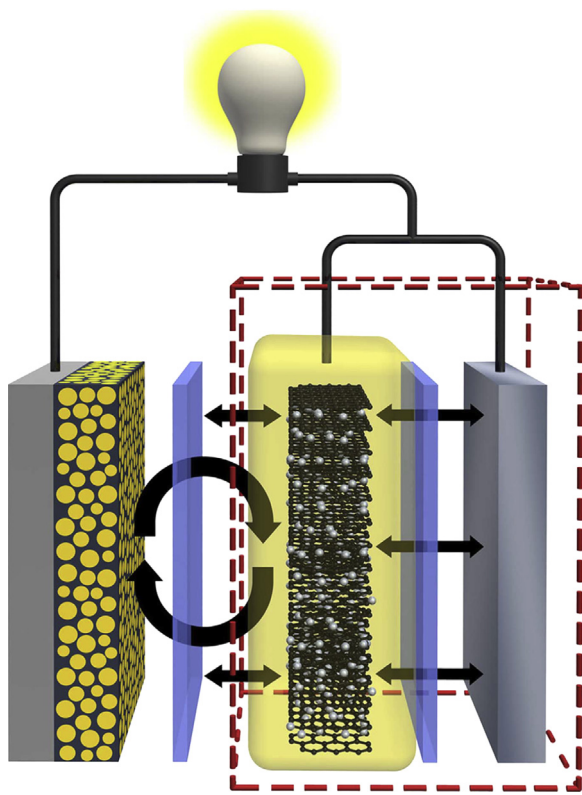


Fig. 10. Schematic of the hybrid anode design with the addition of a graphite layer in front of the lithium metal to minimize the sulfur side reactions. Reproduced from Ref. [196] with permission of Nature Publishing Group.

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